

# Flame Suppression By Sprays Of Aqueous Solutions Containing Phosphorus

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## INTRODUCTION

With the ban on the manufacture of  $\text{CF}_3\text{Br}$  (halon 1301), a common fire suppressant, due to its high ozone-depletion potential, there has been widespread interest in finding a viable substitute [1-4]. A search for a drop-in replacement has not yet been successful, and as an alternative, liquid-phase or solid-phase agents are currently being considered. Delivering the agent as an aerosol broadens the range of potential agents available, but also makes it more difficult to predict flame suppression effectiveness. Aside from gas-phase chemical and physical effects upon vaporization and/or volatilization of the aerosol, these agents may exhibit increased flame suppression because of various phenomena related to the presence of a second phase. These phenomena include enhanced radiative heat transfer, enthalpy of vaporization and/or volatilization, and heterogeneous reactions involving flame radicals [5,6]. Particle or droplet delivery also introduces uncertainty in the amount of agent present in the gas phase in the flame. Gas-phase loading in the flame can be reduced from the amount in the air stream because of insufficient time for vaporization/volatilization in the flame, and can be either reduced or increased when aerosol trajectories differ from air streamlines [7]. Differences in the location in the flame where the agent reaches the gas phase, and possible nonuniform loading after vaporization/volatilization have an unknown effect on flame suppression effectiveness. In this work, a comparison is made between additives introduced as aqueous solutions and those in the vapor phase. The experiments are designed to eliminate several of the sources of uncertainty in agent effectiveness described above.

Most of the work with solid-phase additives has focused on  $\text{NaHCO}_3$  [8-10] or  $\text{KHCO}_3$  [11]. These studies have all shown these powders to be more effective than  $\text{CF}_3\text{Br}$  at fire suppression. The effectiveness is highly dependent on the size of the particles, with smaller particles having a greater effect than larger ones on a per mass basis. This difference is attributed to the large particles not being completely consumed in the flame zone. This critical diameter above which the particles are not completely consumed is experiment dependent, and found to be  $\sim 5\mu\text{m}$  for  $\text{NaHCO}_3$  in a counterflow burner [8]. The high level of effectiveness from the small particles is believed to be due to a chemical effect of the agent in the gas phase [5].

In the liquid phase, water mists have been gaining in popularity, due to their relatively high level of effectiveness and zero toxicity [7,12-15]. Water mist has been shown to be more effective, on a per mass basis, than  $\text{CF}_3\text{Br}$  [15]. However, water only acts as a physical agent in suppressing the flame. A variation of the traditional water mist is an “enhanced” water mist, a water solution containing a compound that, through effects on flame chemistry, increases the fire suppression effectiveness over that of pure water [16-18]. A concern with adding a chemical agent is that toxicity of the solution will be higher than of pure water. However, as the chemical agent’s effectiveness is supplemented by that of the water accompanying it in an enhanced water mist, its required concentration may be acceptably low from a standpoint of toxicity.

A few experimental studies have been done with enhanced water mists, namely water solutions of  $\text{NaOH}$  or  $\text{NaCl}$  [17-19]. These show enhancement of flame suppression compared to pure water. For example, a water mist enhanced with 18%  $\text{NaOH}$  by mass was shown to be several times more effective than pure water in an opposed-jet, non-premixed methane-air flame [19]. The mechanism by which an enhanced water mist results in improved suppression over neat water is not completely understood. It is believed that there is a chemical effect by the solute, and possibly also a physical effect from the droplets or residual particles. The relative magnitudes of these effects have not been determined. In our study, the flame suppression

effectiveness of water solutions containing phosphorus was investigated experimentally and contributions of the chemical and physical effects evaluated.

Phosphorus compounds have been studied previously in the gas phase and shown to be highly effective flame suppressants [20-23]. Since low vapor pressure hinders the introduction of the phosphorus-containing compounds (PCCs) in the gas phase, their use in practical fire fighting situations is limited. However, experimental studies [20] have shown that the effectiveness of the gas-phase PCCs are independent of the form of the parent compound, expanding the options of PCCs available. The phosphorus atom produces phosphorus-containing radicals, such as HOPO and HOPO<sub>2</sub>, which catalyze the recombination of the important combustion radicals, H, OH and O, slowing the overall reaction rate and thus suppressing the flame [21,23,24]. An earlier study used laser-induced fluorescence to measure OH radical levels in a non-premixed flame with and without dimethyl methylphosphonate [22,25]. These measurements show a decrease in the OH level with the addition of this PCC, supporting the hypothesis of catalytic radical recombination. Thus, with the inhibition due primarily to the central phosphorus atom, then the use of liquid-phase PCCs, as enhanced water mists, is a possible alternative.

In the current study, a non-premixed methane-air flame was used to investigate the effectiveness of several PCCs. These compounds are delivered into the air stream either in the vapor phase, as a fine mist of neat liquid, or as a fine mist of aqueous solution. Neat liquids and aqueous solutions involving the liquid PCC dimethyl methylphosphonate (DMMP) are expected to evaporate fully before the flame. For other compounds introduced as aqueous solutions, a small residual particle is expected to remain upon evaporation of the water from the solution. Assuming all of the phosphorus compounds have similar chemical fire suppression effectiveness once they are in the gas phase, fire suppression effects due to the particle phase can be investigated.

Experiments were performed using an opposed-jet burner apparatus. This configuration has been used extensively with experimental, numerical, and analytical techniques to evaluate the performance of flame suppressors [4,26,27]. The counterflow configuration is useful in studying flame-suppressing additives as the flame is thermally isolated and quasi-one-dimensional along the centerline [28,29]. Flame strength can be characterized by the global strain rate at extinction [30,31].

## EXPERIMENTAL METHOD

The flame suppression effectiveness of several PCCs, introduced either in the vapor phase or as droplets of neat liquid or aqueous solution, was investigated. The compounds are listed with their CAS number and chemical structure in Table 1, along with the form in which they were introduced into the burner system. The compounds studied were: distilled water, dimethyl methylphosphonate (DMMP), orthophosphoric acid (OPA), phosphonic acid, phosphorous acid, diethyl methylphosphonate, and dimethyl phosphite. Each of the phosphorus acids was in a 1.6% molar solution in water, and DMMP was introduced both in a 1.6% aqueous solution and as a neat compound, in separate experiments. As shown below, essentially all water and DMMP evaporate before the oxidizer mixture leaves the burner nozzle. In the case of the acid solutions, a solid residual particle remains, while for DMMP and water, the mixture entering the flame is entirely gas-phase. The acid compounds were chosen because they have been seen, through in-situ sampling and GCMS analysis [32], to be decomposition products of DMMP, a PCC shown to be an effective flame suppressant [20,21]. These compounds are also attractive

because of their heating value and because, unlike many PCCs, they are not believed to be neurotoxic. The acid compounds are expected to produce dry or nearly dry solid particles upon evaporation of the water in the solution; all other compounds enter as gases.

Table 1

| Compound                          | Form                                 | CAS number | Molecular formula        |
|-----------------------------------|--------------------------------------|------------|--------------------------|
| Orthophosphoric acid (OPA)        | aqueous solution                     | 7664-38-2  | $P(=O)(OH)_3$            |
| Phosphorous acid                  | aqueous solution                     | 10294-56-1 | $P(OH)_3$                |
| Phosphonic acid                   | aqueous solution                     | 13598-36-2 | $P(=O)(H)(OH)_2$         |
| Methylphosphonic acid             | aqueous solution                     | 993-13-5   | $P(=O)(CH_3)(OH)_2$      |
| Distilled water                   | neat liquid, vapor                   | 7732-18-5  | $H_2O$                   |
| Dimethyl methylphosphonate (DMMP) | neat liquid, vapor, aqueous solution | 756-79-6   | $P(=O)(CH_3)(OCH_3)_2$   |
| Diethyl methylphosphonate (DEMP)  | vapor                                | 683-08-9   | $P(=O)(CH_3)(OC_2H_5)_2$ |
| Dimethyl phosphite (DMP)          | vapor                                | 868-85-9   | $P(=O)(H)(OCH_3)_2$      |

For compounds introduced in the liquid phase, the experimental apparatus consists of a nonpremixed counterflow burner equipped with a system for adding the liquid agent into the oxidizer stream: a nebulizer mounted in a large chamber, leading into temperature-controlled tubing. The apparatus is shown in Figure 1. Its key features are small droplet size, large residence time of the reactant stream under temperature-controlled conditions, and the availability of an accurate procedure for measuring losses to surfaces within the feed system. These features lead to a well-characterized state of the reactant mixture at the exit of the burner tube, and well-defined gas-phase loading of chemical agent at the flame, as documented below. In the case of vapor-phase additives, the nebulizer and chamber are replaced by a syringe pump and further length of heated tubing, as previously described [20].

## Burner

The flame is produced near the stagnation plane of counterflowing streams of fuel and oxidizer. This opposed-jet burner geometry has been detailed previously [20]. As in previous experiments, the reactant nozzles are straight glass tubes (0.98cm I.D.) with a separation distance of 0.95cm. Methane (99% pure) fuel flows from the lower nozzle and the oxidizer, a primary standard mixture of  $21 \pm 0.2\%$   $O_2$  with  $N_2$  balance, flows through the upper nozzle. The temperature of the reactant streams 10cm upstream from the exit of the nozzles are actively maintained at  $360 \pm 1K$ .

The relative flame strength is characterized by the global strain rate at extinction, calculated using the following expression:

$$a_q = \frac{2V_0}{L} \left( 1 + \frac{V_F \sqrt{\rho_F}}{V_O \sqrt{\rho_O}} \right) \quad \text{Eq. 1}$$

In Eq. 1, L refers to the separation distance between the nozzles, V is the average stream velocity at extinction,  $\rho$  is the stream density and the subscripts O and F refer to oxidizer and fuel respectively. Plug flow boundary conditions at the nozzle exit are assumed. This expression, derived by Seshadri and Williams [33], is referred to as the global extinction strain rate. To

determine dopant suppression effectiveness, the global extinction strain rate was measured as a function of additive loading. For a compound, this reduction is expressed as the global extinction strain rate for a known loading normalized by the undoped value, or  $a_q/a_{q0}$ .

For a fixed nozzle separation  $L$ , the reactant velocities are increased until the critical strain rate is achieved and the flame is extinguished. In most studies [4,34], both the fuel and oxidizer velocity are increased proportionally such that the flame or stagnation plane is maintained near the center of the burner. Because the addition of a liquid-phase dopant is via a mass flow syringe pump, changing the doped reactant flow rate would change the dopant loading, leading to transients of a fairly long time scale (several minutes). This difficulty is circumvented by performing extinction measurements holding the doped reactant (oxidizer) stream fixed, and only varying the undoped (fuel) stream flow rate. The flame and stagnation plane move in this method, but for a range of known flame positions, the global extinction strain rate was found to agree within  $\pm 2\%$  [20]. A validation of this technique with aqueous solutions was performed.

### **Generation and characteristics of droplet mist**

A small glass nebulizer is used to deliver the liquid-phase dopant as a fine mist of droplets. This High-Efficiency Nebulizer (HEN), manufactured by J.E. Meinhard Assoc., is detailed in Figure 2. Liquid is introduced via a programmable syringe pump. Part of the oxidizer stream is supplied as the nebulizing gas at a flow rate of 1.00 SLM. This flow rate allows for sufficient aerodynamic break-up of the liquid stream into a fine mist. The HEN is mounted at the top of a large heated chamber (15cm I.D., 18cm long) located approximately 75cm upstream of the flame. Unfortunately, the presence of the chamber induced flow fluctuations that perturbed the flame. To dampen these fluctuations, a small diameter (3.2mm I.D., 7.6cm long) tube was placed between the chamber and reactant flow tube. In this configuration, measurements of the undoped extinction strain rate with and without the chamber and were performed and found to be within  $\pm 3\%$ . The undoped global extinction strain rate is measured to be  $322 \text{ s}^{-1}$ .

In order to investigate several different compounds at several different loadings, it is important for the droplets produced in each case to be similar. The droplets should also be small enough that they will have completely evaporated prior to reaching the flame. Measurements of droplet diameters were performed with a phase-Doppler particle anemometer (PDPA, Dantec FlowLite Fiber PDA). The HEN was not mounted in the apparatus for the PDPA measurements; rather, it was mounted in an enclosed chamber with good visual access. Droplet diameters were measured for a variety of concentrations and flow rates of phosphorous acid, as well as for a single set of conditions for water, DMMP, OPA, and phosphonic acid. Measurements by the PDPA were performed 1.3cm downstream of the HEN tip, with 1.00 SLM of nebulizing gas. Typical histograms for two different cases are shown in Figures 3a and 3b; with the uncertainty of the PDPA is reported to be as  $\pm 2\mu\text{m}$ . As can be seen in the histogram, all of the droplets are less than  $20\mu\text{m}$  in diameter and the size distribution for the two are very similar. A comparison of Sauter mean diameters from the different cases is given in Figure 4. The error bars represent one standard deviation of the droplet size determination.

### **Evolution of droplet mist**

For droplets of neat liquids and DMMP/water solutions, complete evaporation upstream of the exit of the oxidizer nozzle is ensured by high temperatures and long residence times. The

chamber is heated electrically, while the temperature of the gas in the burner tube is actively controlled to  $360 \pm 1$  K by electric heating of the surrounding sheath gas. The average residence time of the droplets is several seconds, while a simple  $D^2$  analysis of the evaporation rate for the maximum droplet size predicts that pure DMMP or water droplets should evaporate entirely within a few milliseconds within the chamber. To confirm complete evaporation, a HeNe laser beam was passed through the reactant stream just below the exit plane of the oxidizer nozzle, and the off-axis forward scatter region was scanned by eye for visible light. For neat solutions, there no observable scattered light, indicating that the additive is in the vapor phase at this point.

For droplets of phosphorus acid solutions, which should produce residual solid particles upon evaporation of water, little quantitative information is available on evaporation rates. However, it is expected that these evaporation times are comparable to those for neat liquids, and that the much longer residence times upstream of the nozzle are sufficient to achieve phase equilibrium between the residual particle and the surrounding gas stream. Whether the compounds under consideration exhibit deliquescence (producing dry residual particles), or whether they retain some water even at low relative humidity is not known. The relative humidity of the air stream is only 2.4% under burner exit conditions, and thus the amount of water retained in the particle at equilibrium is likely to be small if not zero.

For all compounds, the active temperature control of the reactant streams is crucial. The agent-laden oxidizer stream is heated externally to maintain its temperature at 360 K. Thus the enthalpy of vaporization of the water is supplied from external sources, and does not contribute to the fire suppression effectiveness of the agent in these experiments. The apparatus is designed to produce a well-defined state for the oxidizer stream at the nozzle exit: phase equilibrium at 360 K, with all phases traveling at the same velocity. This well-defined state is highly desirable for computational modeling.

When residual particles are present, their size affects their ability to follow gas streamlines in a decelerating flow. Size also determines whether in-flame volatilization is fast enough to release the entire mass of chemical agent into the gas phase. Clearly, small particles are desirable to produce well-defined gas-phase agent loadings for both of these reasons. The residual particle diameter can be estimated from the measured droplet size distribution by assuming each droplet loses all of its water and becomes a spherical particle with density equal to that of the pure solid PCC. This estimate yields a Sauter mean particle diameter of  $3\mu\text{m}$ , and a maximum particle diameter of  $7\mu\text{m}$ . Although rapid heating of solution droplets has been shown to produce highly nonspherical residual particles [35], the assumption of a spherical particle gives conservative results for both drag and volatilization rates. The current estimate of particle size will not be conservative, however, if significant coalescence of particles occurs downstream of where the droplet size distribution was measured.

At typical extinction strain rates in our burner, Stokes numbers for estimated mean and maximum particle sizes for 1.6% OPA are calculated to be 0.02 and 0.1, respectively. These low numbers, representing the ratio of droplet response time to flow residence time that particles are able to follow gas streamlines, avoiding the complications of nonuniform loading described by other investigators [7]. The estimated particle sizes are well below  $30\mu\text{m}$ , the diameter for critical damping for our flow conditions, calculated using the expression developed by Li estimates for critical damping [36]. Thus the particles should not oscillate in the flowfield. Another indication of how well the particles follow the gas streamlines is from a comparison of the drag force (assuming Stokes' flow) with the gravitational force. This ratio is on the order of

200 for 7 $\mu$ m particles and 2000 for 3 $\mu$ m particles. Thus, the particles will quickly reach the velocity of the gas and not be externally influenced by the gravitational field.

Viewing of scattered laser light, described above, provides information about the completeness of particle volatilization in the flame. Experiments were performed with a mist of 1.6% OPA introduced by HEN, with a strain rate 10% below the extinction value. Scattered light was observed when the laser beam was positioned just below the exit plane of the oxidizer nozzle confirming the ability to detect residual particles. No scatter was observed below the flame region, indicating that the particles are small enough to be consumed in the flame. In this second experiment, care was taken to position the laser beam above the stagnation plane: particle scattering was seen in this region at the same reactant flow rates, but with no flame present.

### Wall losses

The chamber housing the HEN was designed to minimize wall losses. The spray leaving the HEN comes out in a cone at a small angle ( $\sim 15^\circ$  half angle), entering a large chamber that has a supplemental oxidizer stream entering near the edge. Even with this chamber, it was not possible to achieve zero wall losses. With solutions, droplets or residual particles appear to be lost to the walls. To quantify the amount of acid PCC lost, the following rinsing procedure was used. A known amount of OPA, in the form of a 1.6% water solution, was sprayed into the apparatus under the same conditions used for the extinction experiments. The chamber and all tubing downstream were then rinsed with a known amount of distilled water. The pH of the wash was measured using an Accumet pH probe, and concentration of OPA was determined from its dissociation constant. The amount recovered was compared to the amount entering, and losses calculated. The net amount of acid PCC delivered to the flame was calculated from the amount lost subtracted from the amount entering through the HEN. Several different flow rates and liquid flowrates were tested, and PCC losses were found to be  $13.8 \pm 0.6\%$  of initial amount delivered. This correction, measured with OPA, is applied to all aqueous solutions other than DMMP. It is assumed that losses occur only for the acid PCC, and that any accompanying water that impinges on the walls is subsequently evaporated. For liquids not producing residual particles, zero losses are assumed. This last assumption was confirmed through extinction experiments with DMMP and water, described in the next section.

## RESULTS

Extinction measurements were performed for two neat substances, H<sub>2</sub>O and DMMP. Figure 5 compares the normalized global extinction strain rate obtained with liquid-phase introduction to that with vapor-phase introduction as a function of dopant loading. The loadings are calculated, for all cases, assuming the dopant is completely evaporated. For the vapor-phase tests, the dopants were added, via syringe pump, into a heated reactant line upstream of the oxidizer flow tube. The vapor-phase tests for DMMP were performed and reported earlier [20]. The same additive loadings were repeated with the dopant introduced in the liquid phase, using the HEN. A lack of light scattering indicated complete evaporation of the H<sub>2</sub>O and DMMP droplets. Figure 5 demonstrates that the normalized global extinction strain rate is independent of the initial phase of the additive. This result is expected, as it is consistent with zero wall losses and complete evaporation of the neat liquid droplets, with the enthalpy of vaporization supplied from outside the reactant stream.

The suppression effectiveness of H<sub>2</sub>O vapor determined here can be compared to literature values obtained with reactants at a slightly lower temperature. Lentati et al. have

numerically investigated the effect of various concentrations of water vapor added to a non-premixed methane-air flame with reactants at 300 K [7]. Roughly linear behavior is observed, with 25% reduction in extinction strain rate at saturation (i.e. with water loading 3.51%). Experiments have also been performed with saturated water vapor at the same temperature [19], finding only a 12% reduction in extinction strain rate. Our experimental loadings, as shown in Figure 5, extend from 4% to 40% of the mole fraction giving saturation at 300 K, and extinction strain rate is linear in that range. Our results are in good agreement with Lentati's calculations over the range in which they overlap. It should be noted, however, that our measurements were made with the reactants at 360K, while the numerical work assumes 300K. Linearly extrapolating our experimental results to 3.51% loading gives a 24% reduction in extinction strain rate, which agrees well with Lentati's calculated value but it is twice Lazzarini's measured value. If water's fire suppression effectiveness decreases at higher loadings, linear extrapolation would not be valid, and values would move towards those measured by Lazzarini.

Experiments were performed comparing H<sub>2</sub>O to 1.6% OPA. The results are given in Figure 6, with the normalized extinction strain rate plotted as a function of molar loading of the H<sub>2</sub>O only. For the case of the PCC, the H<sub>2</sub>O loading is calculated from subtracting the phosphorus contribution (1.6%) from the total dopant loading. It assumed all of the water is delivered to the flame. A linear regression on the slopes indicates that 1.6% of phosphorus approximately doubles the effectiveness of pure H<sub>2</sub>O vapor, per mole of H<sub>2</sub>O delivered. This result gives support for the use of an enhanced water mist to substantially increase the effect of pure water, without introducing large quantities of a chemical substance.

To test whether the chemical structure of the parent compound is important, several PCCs were introduced to the flame and suppression effectiveness compared. The compounds tested were: four 1.6% (molar) aqueous solutions (DMMP, OPA, phosphorous acid and phosphonic acid), introduced via the HEN, and three neat substances: dimethyl phosphite (DMP) and diethyl methylphosphonate (DEMP) introduced as vapors using the technique documented previously [20], and DMMP introduced as a liquid through the HEN. The corresponding published [20] vapor phase DMMP results are also included. All results are plotted versus the "phosphorus loading," or the mole fraction of phosphorus-containing molecules in the oxidizer stream after complete vaporization of the additive. In the case of the neat compounds, this quantity is simply the mole fraction of the additive (after vaporization in the case of DMMP); wall losses are assumed to be zero as described above. For the DMMP/water solution, the phosphorus loading is the mole fraction DMMP in the oxidizer stream, assuming total vaporization of DMMP and water. Here again, zero wall losses are assumed. For the phosphorus acid solutions, the phosphorus loading is calculated as for the DMMP/water solution, and then reduced by 13.8% to correct for wall losses. (See Wall Losses section.) Note that each PCC molecule contains exactly one phosphorus atom, and so these loadings represent the number of moles phosphorus atoms per mole oxidant mixture.

The results fall into two broad bands: the neat substances and the substances introduced as water solutions. The water solutions have steeper slopes, implying higher flame suppression effectiveness per phosphorus loading. This difference is due to the fire suppression contribution from the water in the solution. The results for the 1.6% solution of DMMP can be used to assess whether DMMP and water have additive effects. Linear regressions of the data in Fig. 5 give values of the slopes of the normalized extinction strain rate vs. mole fraction for neat DMMP and H<sub>2</sub>O. A weighted average of these two numbers yields a predicted "effectiveness" of a 1.6% solution of DMMP in water to be 5% more than the actual effectiveness of the solution. Thus,



one can assume additivity of effectiveness is accurate under the conditions of the current experiment. It is expected that synergistic rather than additive behavior will be seen at higher H<sub>2</sub>O loadings, as the effectiveness of chemical agents has been observed to increase with decreasing temperatures [25,37]. However, in our experiments, the change in the adiabatic flame temperature by the amount of water added is not significant enough to result in an observable change in the extinction strain rate. Addition of 1.5% H<sub>2</sub>O changes the adiabatic flame temperature by only 20K; according to previous work, this change would increase the effectiveness of the chemical compound by only approximately 10% of that from a flame without an inert dopant [38]. This difference is within the scatter of the data.

Within the group of neat substances, all PCCs exhibit similar reduction of the global extinction strain rate, per mole PCC. There is a maximum difference of about 25% in slopes obtained by linear regression for these compounds. Similarly, among the phosphorus acids (OPA, phosphonic acid, and phosphorous acid), there is a maximum difference of about 20%. When the data for the DMMP solution is included, the spread is larger: there is a maximum difference of 45% in slopes in the set of water solution data (between DMMP and OPA). The possible significance of the difference between results for the DMMP solution (which vaporizes entirely) and for phosphorus acid solutions (which produce residual particles) is discussed below.

Within the group of neat substances, or within the group of phosphorus acids, differences in the chemical structure of the molecule bearing the phosphorus atom introduce only fairly small differences in fire suppression effectiveness. Experimental uncertainty, differences in heating values of the compounds, and differences in the kinetics leading to the formation of the phosphorus-containing species that participate in radical recombination cycles, may contribute to these small differences in effectiveness. In addition, for the phosphorus acids, differences in characteristics of residual particles, for example volatilization rates or radiative properties, may also contribute to the scatter.

The results for the DMMP solution and acid solutions allow an evaluation of the importance of the effects of residual particles on flame suppression. As mentioned earlier, the DMMP solution will completely vaporize before reaching the flame, while the acid solutions will result in residual particles. Whether the presence of particles is likely to increase or reduce flame suppression effectiveness is not clear. Enhancement of radiative heat transfer, enthalpy of volatilization, and reactions on particle surfaces before the particle is volatilized can all be expected to increase effectiveness over that of a purely gas-phase additive. The fact that finite volatilization rates may release agent into the gas phase relatively late in the flame may decrease effectiveness, and the possibility of nonuniformity in loading has an unknown effect on flame suppression.

All the phosphorus-based acid solutions are more effective than the DMMP solution, but the differences are not large. The largest difference is between OPA and DMMP, whose slopes differ by about 45%, as shown more clearly in Figure 8. Error bars are included on the data points to represent scatter in the extinction measurement and uncertainty in flow measurements. Uncertainties in the loading are not included, as they are negligible on the scale of this figure.

Gas phase effects, e.g. differences in kinetics or heating value, may contribute to the moderate observed difference in effectiveness of OPA and DMMP solutions. To estimate the magnitude of the effect of the fuel content of an additive, extinction strain rate measurements were performed with a small amount (400 ppm) of iso-octane added to the air stream of a methane/air flame. Iso-octane has a heating value (on a molar basis) that is ~2.3x that of DMMP, while OPA has a small negative heating value (assuming the phosphorus product is

P<sub>4</sub>O<sub>10</sub> [39]). As iso-octane was shown to be a flame promoter [20], correcting for heating value effects would bring OPA and DMMP results into better agreement. However, the correction is not large: if extinction strain rate increases linearly with heating value, the heating value effect would account for less than one fifth of the total difference in effectiveness between DMMP and OPA. Gas-phase kinetic differences may be significant compared to the remaining discrepancy of 40% between DMMP and OPA; even when corrected for heating values, gas-phase PCC effectiveness differs by as much as 28% among the compounds tested here. Because it is not known which compound's kinetics is more favorable to flame suppression, it is not known if the true particle effect is larger or smaller than 40%.

Taking the 40% difference between DMMP and OPA effectiveness as an estimate of the magnitude of particle effects, we conclude that the net particle effect appears to be smaller than the gas-phase chemical effect of the phosphorus. Under conditions reported here, the particles would account for less than one third of the total suppression of the solution, compared with the gas-phase chemical effect that is responsible for about one half of the total suppression. If the comparison were made between DMMP and the other acid solutions, the particle effect would be even smaller.

## SUMMARY

An investigation of the flame suppression for water and multi-phase phosphorus-containing compounds (PCCs) was performed. To do so, a technique to introduce an additive as a fine mist of droplets into an opposed-jet non-premixed flame was developed and validated. A High-Efficiency Nebulizer (HEN) was used to produce the droplets, and droplet size measurements using a phase Doppler particle anemometer established that the size distribution of the droplets is independent of the compound and liquid flow rate used. This allows wide application of the HEN for study of different potential additives. Key features of the system are small droplet size, large residence time of the reactant stream under temperature-controlled conditions, and the availability of an accurate procedure for measuring losses to surfaces within the feed system. These features lead to a well-characterized state of the reactant mixture at the exit of the burner tube, and well-defined gas-phase loading of chemical agent at the flame. A comparison of the flame suppression effectiveness of PCCs introduced in the liquid and gas phase is made. This technique does not study the effect of droplets on the flame; however, it does allow investigation of the physical effect of residual particles formed from the evaporation of droplets.

Experimental results indicate a significant reduction in global extinction strain rate with the addition of pure water vapor (10% reduction at 1.5% molar loading), in good agreement with numerical results. With the addition of a small amount (1.6% molar) of PCC in water solution, this reduction doubles. It is also shown that the effectiveness of a PCC/water solution can be obtained by linear addition of the effectiveness of the components. Experimental comparisons among several different PCCs, introduced in the liquid and gas phases, show that the form of the parent compound is relatively unimportant in suppression effectiveness. For our experimental conditions, the physical effect of the residual particles on the flame appears to be less than that from the gas-phase chemistry.

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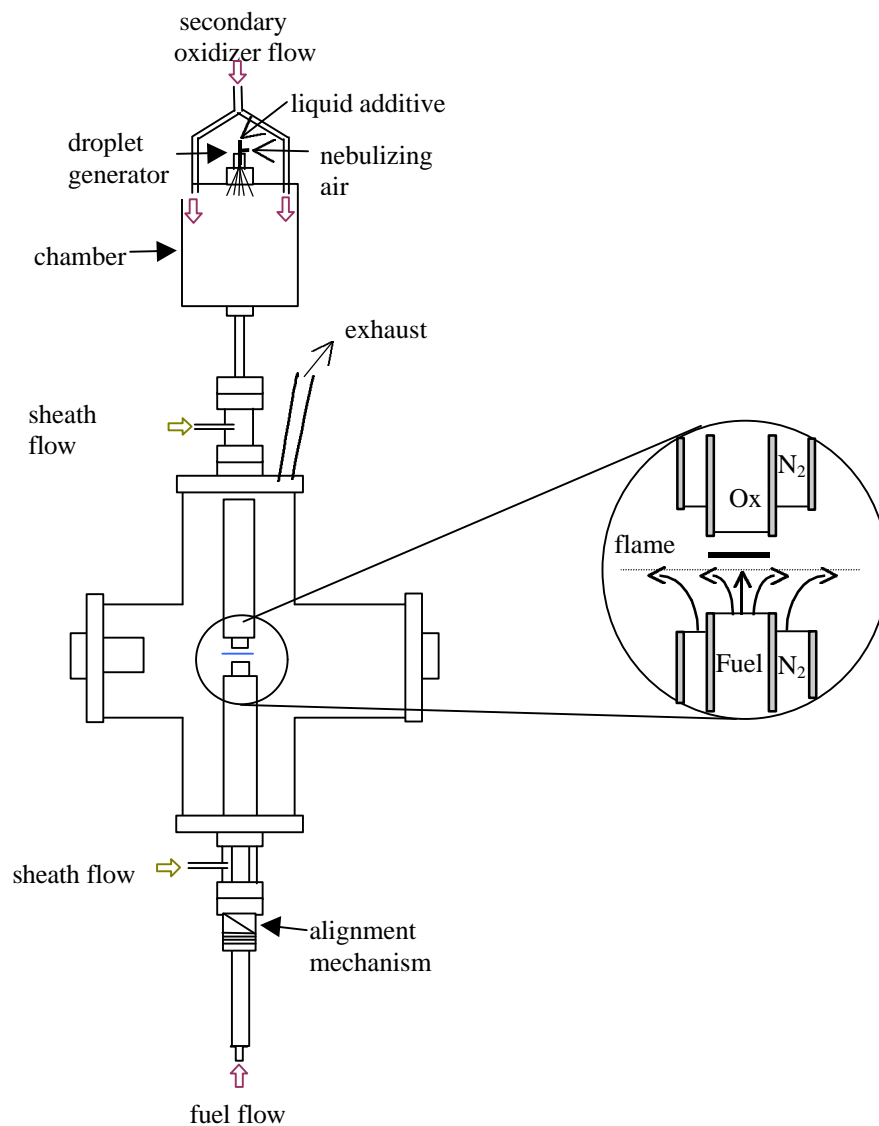
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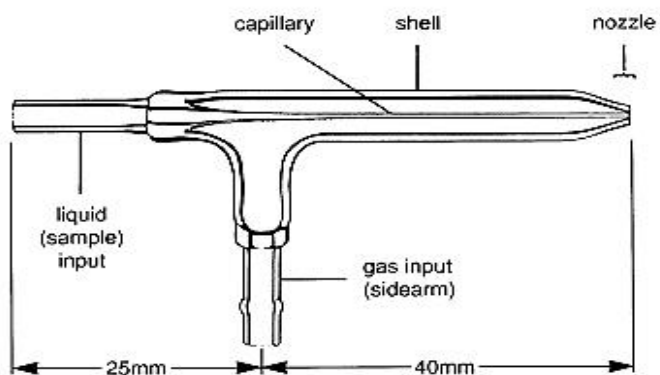
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## Figure Captions

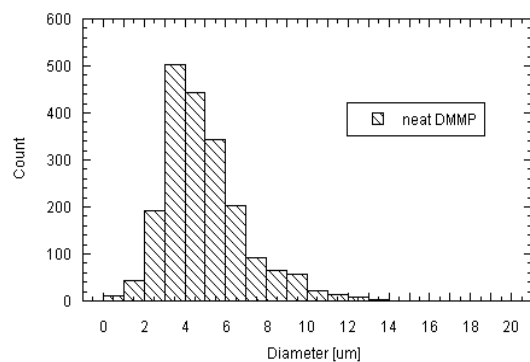
- Fig. 1. Schematic of experimental apparatus with opposed-jet burner, droplet generator and chamber.
- Fig. 2. Droplet generator, known as the High-Efficiency Nebulizer (HEN).
- Fig. 3. Histogram of two different compounds from PDPA measurements of 2000 droplets. The liquid flow rate for both compounds was 25 $\mu$ L/min with 1.00 SLM of nebulizing air.
- a) neat DMMP
  - b) 1.6% (molar) aqueous solution of OPA
- Fig. 4. Sauter mean diameter, measured by PDPA, as a function of liquid flow rate. Under conditions in this paper for aqueous solutions of PCCs, 25 $\mu$ L/min corresponds to a total loading of 1.50%. The various compounds tested were: 7.5% phosphorous acid, 1.6% orthophosphoric acid, 7.5% phosphonic acid, 7.5% methylphosphonic acid, neat DMMP, 4.3% DMMP, and neat H<sub>2</sub>O. All concentrations are molar based in an aqueous solution. Error bars represent one standard deviation in the diameter measurements of 2000 droplets.
- Fig. 5. Normalized global extinction strain rate of neat DMMP and H<sub>2</sub>O, as a function of dopant loading. The dopant was introduced either as a spray via the HEN (liquid phase) or in the vapor phase upstream of the oxidizer flow tube. Loadings are given as the mole fraction of dopant assuming complete vaporization.
- Fig. 6. Comparison of normalized global extinction strain rate as a function of H<sub>2</sub>O loading (assuming complete vaporization) due to addition of neat H<sub>2</sub>O and a 1.6% (molar) aqueous solution of OPA.
- Fig. 7. Comparison of normalized global extinction strain rate as a function of phosphorus loading for several different phosphorus-containing compounds. DMP, DMMP and DEMP are all neat compounds, with DMP and DEMP introduced in the vapor phase. All other compounds, including 1.6% (molar) aqueous solutions of DMMP, orthophosphoric acid, phosphorous acid, phosphonic acid, and methylphosphonic acid, are introduced in the liquid phase via the HEN. The phosphorus loading for the acid solutions have been corrected for wall losses.
- Fig. 8. Normalized global extinction strain rate for 1.6% molar aqueous solutions of DMMP vs. OPA as a function of phosphorus loading. Error bars indicate scatter in data and uncertainty in flow measurement.



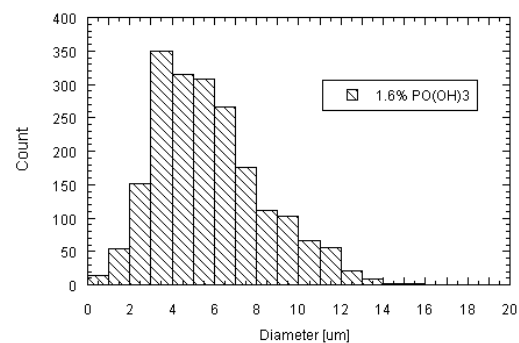
**Figure 1**



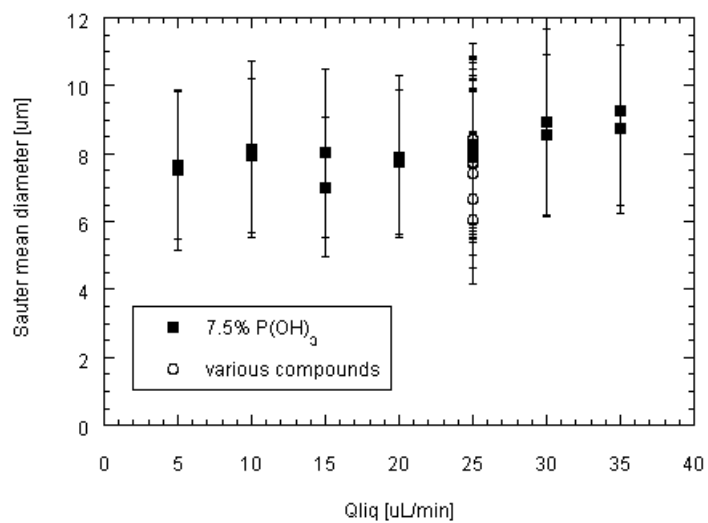
**Figure 2**



**Figure 3a**

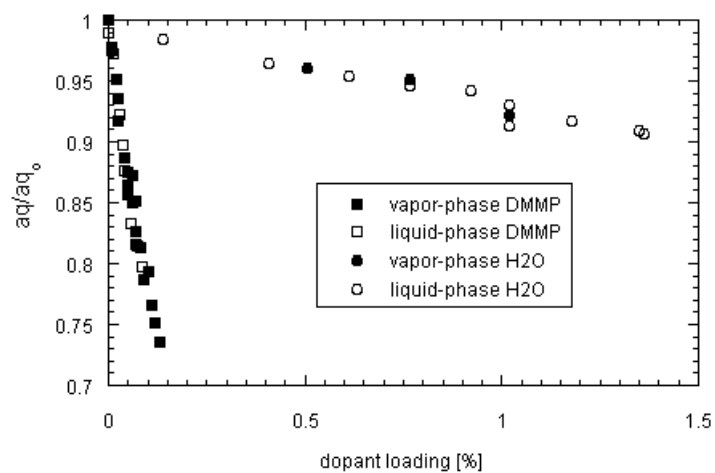


**Figure 3b**

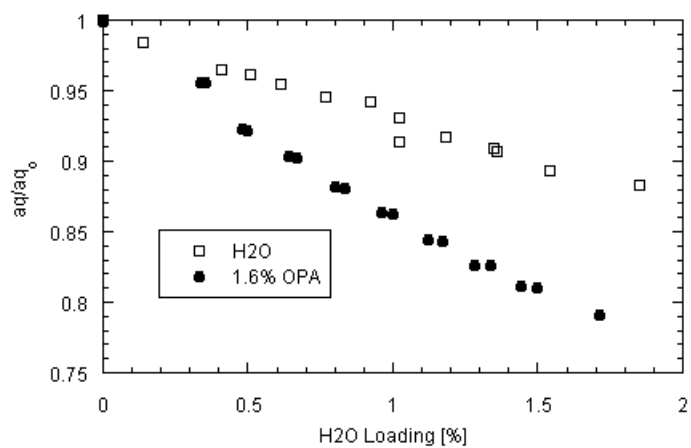


**Figure 4**





**Figure 5**



**Figure 6**

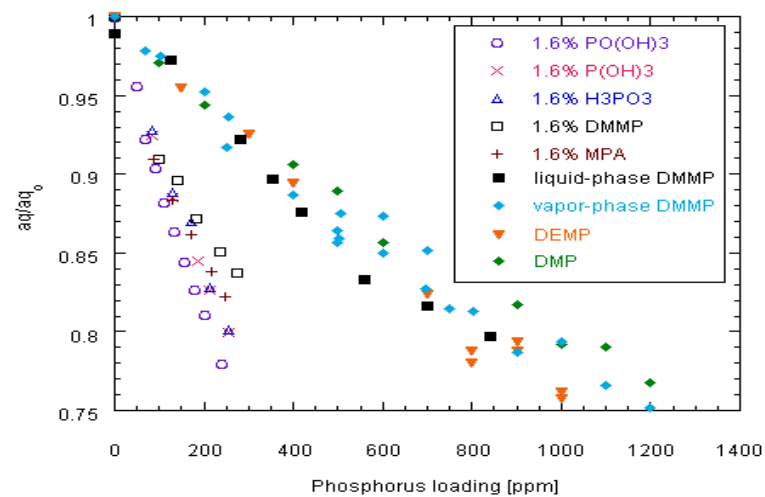


Figure 7

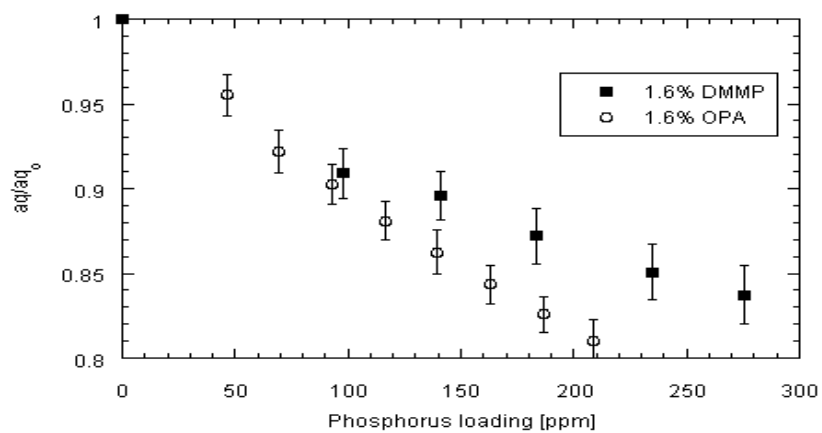


Figure 8